



Effect of aqueous Si/Mg ratio and pH on the nucleation and growth of sepiolite at 25 °C

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Abstract

Sepiolite [$\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$] is a trioctahedral 2:1 Mg-silicate that has been often used to reconstruct the evolution of sedimentary environments and facies in the geological record. To date, however, the reaction paths underlying sepiolite formation are poorly constrained and most of the existing models are based on empirical observations. In order to shed light on the mechanisms controlling the formation of this mineral phase, in the present study, sepiolite was precipitated at 25 ± 1 °C from modified seawater and MgCl_2 solutions undersaturated with respect to brucite and amorphous silica. Although a suite of hydrous Mg-silicates, such as kerolite, saponite, stevensite and talc, were oversaturated in the solutions at a higher level relative to sepiolite at any time of reaction, poorly crystallized, aluminous sepiolite was the only precipitate after 91 days. The precipitated sepiolite [$\text{Mg}_{3.4-3.8}\text{Al}_{0.1-0.4}\text{Si}_{5.9-6.0}\text{O}_{15}(\text{OH})_2 \cdot n\text{H}_2\text{O}$] shares a number of structural and chemical similarities with natural sepiolite, such as a fibrous crystal shape and an atomic Si/(Si + Mg+Al) ratio of ~ 0.61 .

The proposed reaction path for the formation of sepiolite is based on the temporal evolution of the chemical compositions of the experimental solution and solids: (i) Nucleation and growth of Al-sepiolite occurred during the first 8 days of the experimental runs via condensation and polymerization of Si–OH tetrahedra onto Mg–Al–O–OH template sheets at a precipitation rate of $\sim 2.19 \pm 0.01 \times 10^{-10} \text{ mol s}^{-1}$. (ii) At decreasing pH and in the absence of $[\text{Al}]_{\text{aq}}$ this intermediate phase transformed into aluminous sepiolite at a slower crystal growth rate of $\sim 1.08 \pm 0.02 \times 10^{-12} \text{ mol s}^{-1}$. This finding explains the high abundances of sepiolite in highly alkaline, evaporitic, lacustrine and soil environments, where the growth rates of sepiolite are considered faster (10^{-11} to $10^{-10} \text{ mol s}^{-1}$, Brady, 1992). We propose that (i) low rates of Mg^{2+} ion dehydration and silica condensation and polymerization at the surface of the initial precipitate, (ii) the formation of MgSO_4^0 aquo-complexes and (iii) the reduced sorption rates of $[\text{Si}]_{\text{aq}}$ and $[\text{Mg}]_{\text{aq}}$ at the active growth sites on sepiolite surfaces at $\text{pH} \leq 8.3$ retard the precipitation of sepiolite in marine-diagenetic environments.

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1. INTRODUCTION

Volumetrically significant abundances of trioctahedral 2:1 Mg-silicates are rather scarce in most Earth's surface environments. An exception is the widespread appearance

of sepiolite [$\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$] and palygorskite [$(\text{Mg},\text{Al})_4\text{Si}_8\text{O}_{20}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$], which unlike the “ideal” 2:1 Mg-silicates, are characterized by a discontinuous octahedral sheet and an inverted tetrahedral arrangement forming pyroxene-like structures (Guggenheim and Krekeler, 2011). These so-called “modulated” phyllosilicates are commonly formed through the direct precipitation from oversaturated solutions (Wollast et al., 1968; Kent and Kastner, 1985; Galán and Pozo, 2011; Tosca and Masterson, 2014),

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although alteration from smectite precursors has been also documented (e.g., Singer, 1979; Guggenheim and Krekeler, 2011). The mineralogy and the chemical composition of sepiolite-palygorskite group minerals is highly sensitive to variations in pH and alkalinity (Siffert and Wey, 1962; Galán and Pozo, 2011), aqueous Si/Mg ratio (Kent and Kastner, 1985; Tosca and Masterson, 2014), temperature (Guven and Carney, 1979; Christ et al., 1973; Clauer et al., 2012), salinity (Torres-Ruiz et al., 1994), redox conditions (Gehring et al., 1994), availability of reactive aluminous phases (Birsoy, 2002; Cuadros et al., 2016) and presence or absence of seed crystals (Christ et al., 1973; Stoessell, 1988). Hence, variations in the distribution and the abundance of these Mg-silicates in the geological record have been used for reconstructing sedimentary environments and facies in modern and ancient epicontinental and inland seas and lakes (Darragi and Tardy, 1987; Torres-Ruiz et al., 1994; Deocampo et al., 2009; Galán and Pozo, 2011; Kadir et al., 2016), soil environments (Callen, 1984; Jones and Galán, 1988; Cuadros et al., 2016) and more rarely in volcanic belts (Bonatti and Joensuu, 1968; Bonatti et al., 1983; Irkeç and Ünlü, 1993) and deep-sea settings (Hathaway and Sachs, 1965; Bonatti and Joensuu, 1968; Bowles et al., 1971).

Numerous field and experimental studies were conducted in order to systematically describe the physicochemical conditions underlying the formation of sepiolite in natural surroundings and under well-defined laboratory conditions. For example, Cole and Hueber (1957), Siffert and Wey (1962), Smirnova et al. (1966) and Abtahi (1985) precipitated a hydrous Mg-silicate phase with a composition similar to that of ideal sepiolite, together with amorphous silica $[\text{SiO}_2 \cdot n\text{H}_2\text{O}]$ and brucite $[\text{Mg}(\text{OH})_2]$ by a sol-gel process. In these works, NaOH or concrete (to establish alkaline conditions) were added to a solution highly oversaturated with respect to amorphous silica and containing various $[\text{Mg}]_{\text{aq}}$ concentrations. In another approach, Wollast et al. (1968) precipitated sepiolite from seawater doped with up to 5 mM of $\text{Si}(\text{OH})_4$ at $\text{pH} \sim 8$ and concluded that pH is a crucial variable for approaching sepiolite-seawater equilibrium. However, in the last five decades only few studies were conducted that aimed at unraveling the reaction pathways, growth rates and thermodynamic equilibria of sepiolite (e.g., Christ et al., 1973; Kent and Kastner, 1985; Stoessell, 1988; Brady, 1992), which altogether showed that solution chemistry is a key parameter in the formation of hydrous Mg-silicates at low temperatures. Recently, Tosca and Masterson (2014) studied the effect of pH, ionic strength and aqueous Si/Mg ratio on the mineralogy and chemical composition of the precipitating Mg-silicate phases at 25 °C. Their results indicate that sepiolite formation is independent of ionic strength but is fostered at aqueous molar Si/Mg ratios from 1.0 to 1.49 and at $\text{pH} \leq 9$, whereas stevensite $[(\text{Na},\text{Ca})_{0.3}\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}]$ and kerolite $[\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}]$ preferentially form at aqueous molar Si/Mg ratios from 0.17 to 1.0 and at $\text{pH} \geq 9$ (Tosca and Masterson, 2014). Thermodynamic considerations for the system $\text{MgO}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}-\text{CO}_2$ further suggest that sepiolite precipitation from solution is favored at high silicic acid

activities; thus close to the saturation with respect to amorphous silica (Jones, 1986; Stoessell, 1988; Birsoy, 2002). Low Al^{3+} activities promote the formation of the non-aluminous phases sepiolite, saponite $[(\text{Ca},\text{Na})_{0.3}(\text{Mg},\text{Fe})_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}]$, stevensite, talc $[\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2]$ and kerolite over montmorillonite $[(\text{Na},\text{Ca})_{0.3}(\text{Al},\text{Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}]$ and palygorskite (Birsoy, 2002). Similar conditions for the formation of sepiolite have been reported from the study of natural sepiolite-depositing environments that are characterized by high Mg^{2+} and silicic acid activities, absence of reactive aluminous phases and $\text{pH} \leq 10$ (Jones and Conko, 2011 and references therein). Under such conditions, sepiolite and palygorskite co-exist with other 2:1 Mg-silicates, brucite, SiO_2 polymorphs, dolomite $[(\text{Ca},\text{Mg})(\text{CO}_3)_2]$ and hydromagnesite $[\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}]$ (e.g., Polyak and Guven, 2000; Galán and Pozo, 2011; Suárez and García-Romero, 2011; Kadir et al., 2016).

To date, significant gaps in knowledge still exist regarding the reaction pathways and crystal growth kinetics characterizing sepiolite formation. Indeed, in the present literature reliable estimates of solubility products and growth rates for a specific Mg-silicate phase are scarce mainly due to the low crystallinity of the precipitates, presence of reactive intermediates and formation of polyphase products (Tosca and Masterson, 2014). In this study, we examine the effect of the aqueous Si/Mg ratio on the potential crystallization pathways of sepiolite, and provide growth rates and solubility data for poorly crystallized sepiolite formed at 25 °C and $\text{pH} \leq 8.3$. The obtained results are of significance for reconstructing the physicochemical parameters occurring during the formation of Mg-silicates in marine-diagenetic settings.

2. METHODS

2.1. Sepiolite precipitation experiments

Sepiolite was synthesized in 1.0 L high-density polyethylene batch reactors by the addition of a $\text{Si}(\text{OH})_4$ stock solution into seawater (experiment SiMg24) or MgCl_2 solutions (experiments SiMg28, SiMg55 and SiMg110) at 25 °C. The $\text{Si}(\text{OH})_4$ and Mg solutions were prepared from analytical grade chemicals ($\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ containing ≤ 0.04 wt.% of Al from SigmaAldrich, and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ from Roth) in ultrapure water (Millipore Integral 3: $18.2 \text{ M}\Omega \text{ cm}^{-1}$). The pH of both solutions was then adjusted to 8.30 ± 0.03 using 0.5 M HCl or 0.5 M NaOH solutions. Both stock solutions were equilibrated with respect to the atmospheric CO_2 level for about 72 h before starting the experiments in order to prevent a pH drift during the experimental runs due to CO_2 uptake from the atmosphere.

In detail, 0.5 L of a 1.95 mmol L^{-1} $\text{Si}(\text{OH})_4$ solution was mixed either with 0.5 L of seawater originally containing 48 mmol L^{-1} of $[\text{Mg}]_{\text{aq}}$ and 0.12 mmol L^{-1} of $[\text{Si}]_{\text{aq}}$ or with 0.5 L of a Mg stock solution (originally containing 2.2 mol L^{-1} of $[\text{Mg}]_{\text{aq}}$) to receive initial molar Si/Mg ratios of 1:24, 1:28, 1:55 and 1:110 at a constant $\text{Si}(\text{OH})_4$ concentration of 0.98 mmol L^{-1} . Accordingly, the experiments are labeled as SiMg24, SiMg28, SiMg55 and SiMg110, where the number indicates the multiple of the $[\text{Mg}]_{\text{aq}}$ relative to $[\text{Si}]_{\text{aq}}$

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